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Ultrasound facilitates and improves removal of Cd(II) from aqueous solution by the discarded tire rubber

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Abstract

Some of the heavy metal ions such as cadmium are toxic and represent as hazardous pollutants due to their persistence in the environment. In this study the ground discarded tire rubber was used for the sorption of cadmium from aqueous solution. The batch sorption tests were conducted to investigate the sorption of Cd(II) by discarded tire rubber in the presence and absence of ultrasound. To assess the capability of sorbent, research parameters such as ultrasonic waves, solution temperature, particle size of ground tire and others were investigated. The experimental data were fitted in Langmuir model better than Freundlich one. Therefore, the former model was applied to the sorption equilibrium in order to determine the maximum metal sorption capacity in the presence and absence of ultrasound. The Langmuir constants were also obtained from the isotherms under different conditions. In the presence of ultrasound the tire rubber was a more efficient sorbent for this pollutant than its absence. According to the results, the internal porous and film diffusions were both effective in the sorption process. The porous and film diffusion coefficients of the ground tire rubber were, respectively, about 1.8 and 2.7 times more in the presence of ultrasound than its absence. The effect of ultrasound on the sorption process could be explained by the thermal and non-thermal properties of ultrasonic field.

Keywords: Ultrasound; Discarded tire rubber; Cadmium(II); Sorption; Langmuir model

1. Introduction

Toxic metals are often discharged into the environment from a number of industrial processes. Cadmium is widely used in industries in operations such as cadmium plating, and the manufacture of alkaline batteries, copper alloys, paints and plastics [1]. This metal is a non-essential and non-beneficial element for plants and animals. Its toxic effects are well documented and diseases such as renal damage, anemia and itai-itai are associated with excess cadmium [2,3]. The drinking water guideline value recommended for this element by World Health Organization (WHO) and American Water Works Association (AWWA) is 0.005 mg cadmium per liter [4]. Various methods exist for the removal of cadmium ions from solution, such as filtration, chemical precipitation, ion exchange, sorption by activated carbon and others. From the viewpoint of economics, these methods are not generally acceptable and different groups have recently focused the research on the use of low cost sorbents such as bagasse sugar [5], hematite [6], perlite [7], starch xanthate [8], sawdust of pinus sylvestris [9] and discarded automobile tires [10]. In this study, finely-ground discarded tire rubber which caused many public health and environment problems [11] has been used as an interesting and cheap medium for the sorption of cadmium from aqueous solution. This was done in the presence and absence of treatment with ultrasound (a variation of pressure or density with frequencies above the human hearing threshold ≈18 kHz). Ultrasound through its mechanical waves, is known to have an effect on the sorption process. Ultrasonic waves strongly affect mass transfer between two phases. It is well understood that ultrasonic waves have a greater efficiency for interface mixing than conventional agitation [12,13]. This behavior could be the reason for the enhancement of the sorption kinetic process [14–17,19].

2. Materials and methods

2.1. Materials

The finely-ground discarded tire rubber with an average particle size of 0.4 mm was prepared from Yazd Tire Company in

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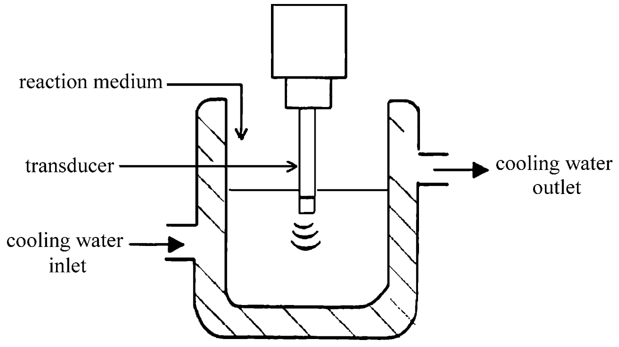

Fig. 1. Scheme of the experimental set-up for the sorption under ultrasonic field.

Iran. Cadmium chloride was from Riedel. A stock solution of cadmium chloride with a concentration of 1000 ppm was prepared in de-ionized distilled water. This solution was diluted as required to obtain the standard solutions.

2.2. *Apparatus*

The ultrasonic irradiation was carried out with equipment operating at 20 kHz (Misonix-XL2020). Ultrasonic waves were emitted from a titanium horn with a diameter of 1.2 cm. The cylindrical sonochemical reactor (volume = 100 ml) was thermostated by a water jacket (Fig. 1). Ultrasonic energy dissipated in the reactor was set generally at 30.0 W and monitored colorimetrically.

2.3. *Analysis*

The cadmium concentration in the solution was determined by spectrophotometry, using a Shimadzu AA-670 atomic absorption spectrophotometer.

2.4. *Procedure*

Batch experiments were conducted by adding 1.0 g of ground tire to 60 ml of cadmium aqueous solution of the desired concentrations at different temperatures, with constant stirring. Equilibrium was reached after 2 h. In order to determine the sorption isotherm of Cd(II) on the powdered tires in an ultrasonic field, the ultrasonic waves were applied continuously on the system from the beginning. Equilibrium was reached after 30 min. The ion concentration retained in the sorbent phase (mg g^{-1}) was calculated by using Eq. (1):

$$q_e = \frac{(C_o - C_e)}{W} V \tag{1}$$

where C_o and C_e are the initial and equilibrium concentrations of metal ion (mg l^{-1}), V is the volume (l), and W is the weight of the sorbent (g) in the mixture.

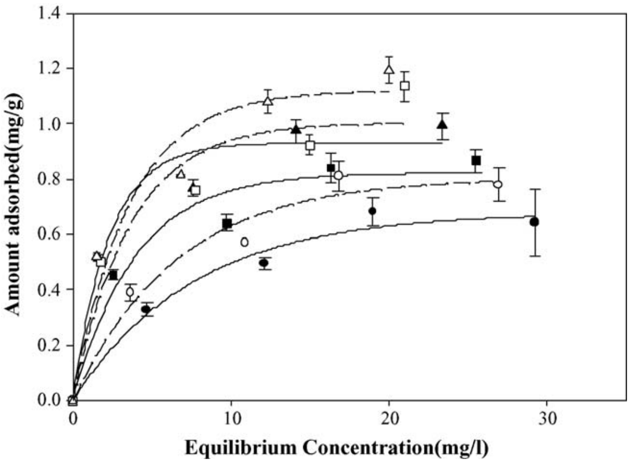

Fig. 2. Sorption isotherms of Cd(II) on the powder tire in the presence and absence of ultrasound: (●) stirring (30 °C); (■) stirring (40 °C); (▲) stirring (50 °C); (○) irradiation (30 °C); (□) irradiation (40 °C); (△) irradiation (50 °C).

3. Results and discussion

3.1. *Sorption isotherms*

Fig. 2 shows the sorption of Cd(II) on the powdered rubber at different temperatures in the presence and absence of ultrasound. The sorption capacity of metal ion was found to be greater in the presence of ultrasound than with simply stirring as a classical method. In both cases, the isotherms exhibited a Langmuir shape. In stirring, the optimum contact time was 2 h and for sonication it was 30 min. This behavior could be explained by the acoustic cavitation (formation, growth and collapse of cavity) which was produced during the sonication. As the bubble collapses, a localized high pressure and temperature are produced in the fluid [18]. In addition, the asymmetric collapse of bubbles in a heterogeneous system produces micro-jets with high velocity on the surface of the sorbent. This action leads to destroying and tearing off the sorbent which may expose new sites and increase the "internal sorption capacity (ISC)" of the powdered tire and also enhancing mass transfer into the pores. These effects can be reasons for increasing the sorption capacity in the presence of ultrasound.

The experimental data were found to fit the Langmuir model better than Freundlich model. The linear form of Langmuir model is represented by Eq. (2):

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_o b}\right) + \left(\frac{1}{Q_o}\right) C_e \tag{2}$$

where q_e is the concentration of the sorbed solute per unit weight of sorbent at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of the pollutant in the mixture (mg l^{-1}) and Q_o corresponds to complete coverage of available sorption sites. The factor b is related to the free energy ($b \propto e^{-\Delta G/RT}$) and the intensity of sorption. A linear plot of (C_e/q_e) versus C_e was employed to find the values of Q_o and b from the slope and the intercept of the line (Fig. 3). Table 1 gives these values with good correlation coefficients.

3.2. *Effect of temperature*

Fig. 4 shows the effect of temperature in the presence and absence of ultrasound. The sorption capacity of rubber increased with increasing temperature in both cases.

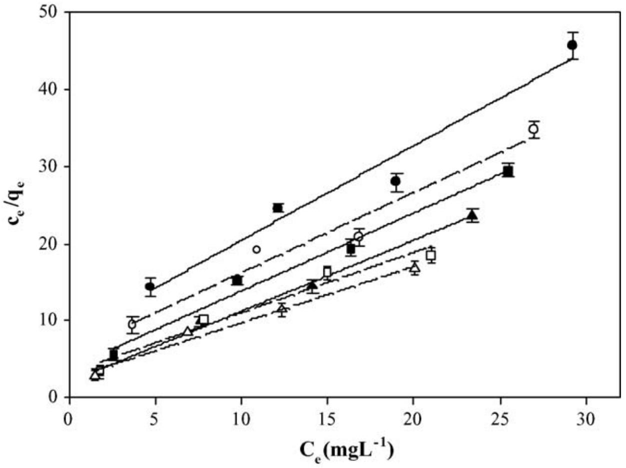

Fig. 3. Langmuir isotherm for Cd(II): (●) stirring (30 °C); (■) stirring (40 °C); (▲) stirring (50 °C); (○) irradiation (30 °C); (□) irradiation (40 °C); (△) irradiation (50 °C).

Table 1
Langmuir constant for the uptake of Cd(II) in the presence of ultrasound and stirring

Method	T (°C)	Langmuir		
		Q_o (mg g^{-1})	b (l mg^{-1})	R^2
Stirring	30	0.82 (±0.11)	0.15 (±0.06)	0.97
	40	0.99 (±0.08)	0.26 (±0.10)	0.99
	50	1.09 (±0.05)	0.44 (±0.14)	0.99
Ultrasound	30	0.96 (±0.13)	0.18 (±0.07)	0.97
	40	1.28 (±0.04)	0.24 (±0.10)	0.98
	50	1.37 (±0.08)	0.30 (±0.17)	0.99

Table 2
Effects of rubber particle size: (30 °C, 20.4 ppm, 30 min)

Ultrasound (sorption%)	Stirring (sorption%)	Particle size (mm)
43.58 (±0.22)	36.79 (±0.35)	0.353–0.500
47.09 (±0.45)	38.44 (±0.75)	0.177–0.250
62.7 (±0.90)	50.90 (±0.95)	0.088–0.125

This indicates that the sorption process was endothermic in nature. The amount of sorption increased from 46.57 to 66.5% in the presence of ultrasound and from 27.47 to 57.28% in the absence of ultrasound during the initial 30 min when the temperature was increased from 30 to 50 °C. This enhancement is felt to be due to the acceleration of the sorption process by the increased movement of metal ions from the bulk solution to the surface of the solid particles at higher temperatures. In addition, in the presence of ultrasound some new active sites might be created.

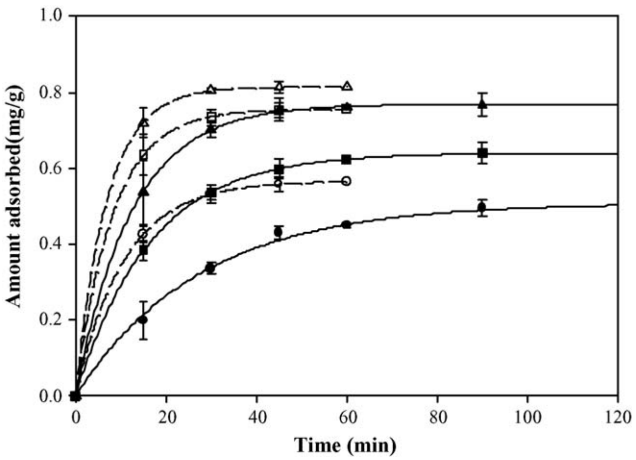

Fig. 4. Effect of temperature on the sorption of Cd(II) in the presence and absence of ultrasound (sorbent = 1g; Cd(II) = 20.4 ppm). (●) stirring (30 °C); (■) stirring (40 °C); (▲) stirring (50 °C); (○) irradiation (30 °C); (□) irradiation (40 °C); (△) irradiation (50 °C).

3.3. *Effect of particle size*

There was an increase in the sorption efficiency when the particle diameter decreased (Table 2). Theoretically, the extent of sorption is related to the concentration of available sorbent sites of the surface. By assuming a spherical shape of the particles, it can be shown that the total surface area is inversely proportional to the diameter of the particles. If only surface sorption sites are utilized for the removal of Cd(II), the sorption capacity for a given sorbent mass should be proportional to ($1/D_P$). The extent of sorption was higher in the presence of ultrasound than stirring. This is related to the asymmetrically collapse of bubbles which lead to the breaking of particles and change the size and morphology of the surface [19]. The breaking of particles produces or opens tiny cracks and channels which can increase the surface area of particle. Therefore, ultrasonic waves can increase the surface area and also the mass transfer which both lead to higher sorption process.

3.4. *Effect of ultrasonic intensity*

Table 3 shows that the sorption increases with increasing acoustic power of the ultrasound. At higher power the cavitation is more intense and leads to enhancement of mass transfer in the system. In addition, under higher power there is a possibility that the surface area becomes increased through destruction of particles. Thus, more new sorption sites may be produced [19]. In one experiment, the ultrasonic intensity was measured with and without rubber. In the medium position, it was 33.5 W cm^{-2} with rubber which is slightly higher than without rubber (32.4 W cm^{-2}). This indicates that the rubber can absorb acoustic energy and this absorption can lead to an increase of sorption. Therefore, these effects of ultrasound (increasing of mass transfer, new sites, and absorption of acoustic energy by rubber) could be reasons for the enhancement of sorption at higher intensity.

Table 3
Effect of ultrasonic intensity and rate of stirring

Sorption (%)	Rate of stirring (rpm)	Sorption (%)	Ultrasound intensity (W cm^{-2})
19.12 (±0.36)	0	23.6 (±1.03)	10.9
30.05 (±0.26)	100	43.57 (±0.39)	32.4
30.45 (±0.26)	300	43.62 (±0.59)	45.4

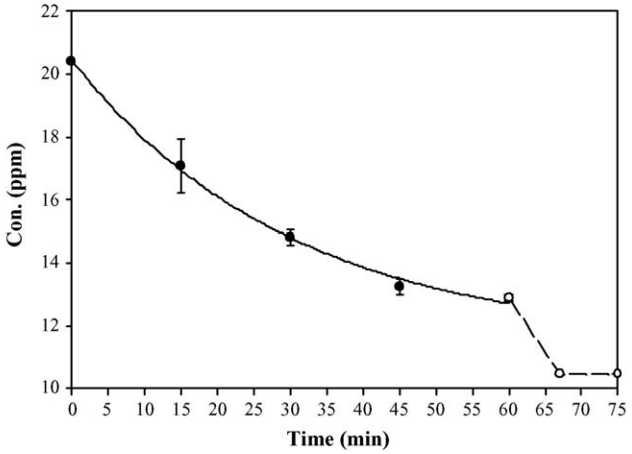

Fig. 5. Combination method ($T = 30\,^{\circ}\mathrm{C}$). (●) Stirring; (○) irradiation.

3.5. Kind of sonication

Most of the experiments in the presence of ultrasound were conducted with continuous sonication from the beginning. In some experiments, however, the mixture of powder and pollutant was stirred for 1 h without ultrasound and then the ultrasonic waves were applied for a final 15 min. According to the data given in Fig. 5, it is apparent that the ultrasonic waves can remove the remaining pollutant from the solution.

3.6. Sorption kinetics

Fig. 4 showed the effect of contact time on the removal of Cd(II) by rubber at different temperatures. The sorption process with only stirring was rapid for the initial 40 min and reached equilibrium after 2 h. In the present of ultrasound, it was rapid for the initial 15 min and reached equilibrium after 30 min. The first-order kinetics of sorption can be described by the Lagergren relation [9]:

$$\log(q_\mathrm{e} - q_\mathrm{t}) = \log q_\mathrm{e} - \frac{k}{2.303}t \tag{3}$$

q_e and q_t are the amounts of sorbed metal ions onto the rubber at equilibrium and at time t (mg g^{-1}), and k is the first-order rate constant of sorption (min^{-1}). A plot of $\log(q_\mathrm{e}–q_\mathrm{t})$ versus t gives a straight line as can be seen in Fig. 6. Therefore, the sorption is first-order in both the presence and absence of ultrasound.

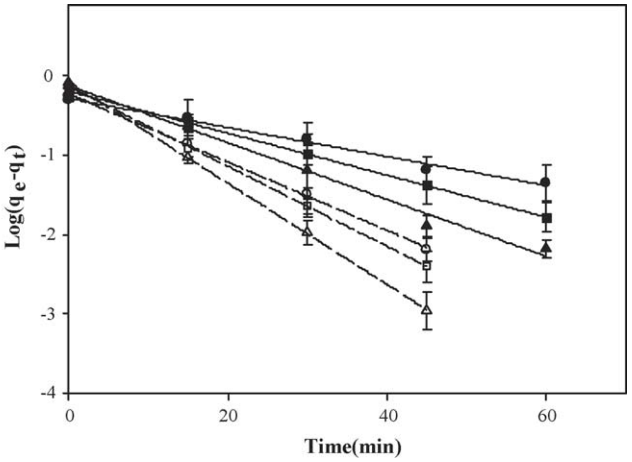

Fig. 6. The first-order kinetic model at different temperatures (Cd(II) = 20.4 ppm; intensity = 32.38 W cm^{-2}). (●) stirring (30 °C); (■) stirring (40 °C); (▲) stirring (50 °C); (○) irradiation (30 °C); (□) irradiation (40 °C); (△) irradiation (50 °C).

As the experimental data fitted properly with the first-order kinetics model, the rate of desorption should be negligible with compare of the rate of sorption. In addition, ultrasound generally has an effect on desorption in cases with lower interaction such as physisorption.

The rate constants were determined from the slope of the plot at different temperatures and the values are presented in Table 4. The sorption rates in the presence of ultrasound were 1.78–2.35 times higher than without ultrasound in the temperature range studied. The activation energies of sorption in the presence and absence of ultrasound were calculated graphically using the Arrhenius equation. The values found are 15.92 and 27.43 kJ mol^{-1}, respectively. This difference could be attributed to the effect of ultrasound on the sorbent. It can probably produce new sites with easier sorption and also the absorption of acoustic energy by rubber as a sorbent can facilitate the sorption process. In addition, ultrasonic cavitation can increase the internal energy of sorbate and lead to an easier sorption process. The mentioned effects are in agreement with the lower activation energy in the presence of ultrasound.

Table 4
Comparison of the first-order adsorption rate constants in the presence and absence of ultrasound

Method	T (°C)	$q_{\mathrm{e(exp)}}$ (mg g^{-1})	$q_{\mathrm{e(cal)}}$ (mg g^{-1})	%Dev	k (min^{-1})	R^2	$\frac{k}{k_{t=30}}$	$\frac{k(\mathrm{us})}{k(\mathrm{st})}$
Stirring	30	0.495	0.521	4.60	0.04	0.98	1.00	2.35
	40	0.640	0.642	0.23	0.06	0.99	1.45	1.90
	50	0.767	0.745	2.80	0.08	0.99	1.95	1.78
Ultrasound	30	0.560	0.590	4.50	0.10	0.99	1.00	
	40	0.757	0.736	2.20	0.12	0.99	1.17	
	50	0.814	0.827	0.73	0.15	0.99	1.48	

$$\Delta q_\mathrm{e}(\%) = \frac{\sum_{i=1}^{N} |[(q_\mathrm{e},i)_\mathrm{cal} - (q_\mathrm{e},i)_\mathrm{exp}]/(q_\mathrm{e},i)_\mathrm{exp}|}{N} \times 100$$

Table 5
Intra-particle diffusion coefficient in the presence of ultrasound and stirring

T (°C)	Stirring			Ultrasound			$K'_w(\text{us})/K_w(\text{st})$
	K_w (mg l^{-1} min$^{-1/2}$)	R^2	$K_w(\text{st})/K_w(\text{st})_{T=30}$	K'_w(mg l^{-1} min$^{-1/2}$)	R^2	$K'_w(\text{us})/K'_{w(T=30)}$	
30	1.049	0.980	1.00	1.805	0.989	1.00	1.72
40	1.564	0.985	1.49	2.630	0.997	1.46	1.68
50	2.209	0.993	2.11	2.983	0.989	1.66	1.35

3.7. Sorption mechanism

In general, sorption may be described as a series of steps by the transfer of solute: (1) from the bulk of solution to the boundary film of sorbent; (2) from the boundary film to the sorbent surface (film diffusion); (3) from the sorbent surface to the intra-particular active sites (porous diffusion); and (4) interaction with the available sites on the internal surface [9]. One or more of the steps mentioned may control the rate of sorption. It has been observed that the ultrasonic waves and associated phenomena such as micro-disturbances of cavitation bubbles near the surface of solid reduce the boundary layer and lead to an increase efficiency of mass transfer [14,19]. If the process is controlled by the external resistance, the plot of $\ln C$ versus time must be linear [14,20]. In both the presence and the absence of ultrasound, this relationship was not observed to fit the data and therefore the external diffusion was not the rate-limiting step. The plot of sorbate uptake versus the square root of time [6] did not pass through the origin. This means that pore diffusion was not the only rate-controlling step. This was further tested by determining the pore diffusion coefficient ($\overline{D}$) from the following equation [9,21]:

$$\bar{D} = \frac{0.03}{t_{1/2}} r_o^2 \quad (4)$$

where $t_{1/2}$ (s) is half-life time of the sorption and r_o (cm) is radius of the sorbent particles. According to Michelsen et al. [6,22], a $\overline{D}$ value in the order of 10^{-11} cm^2 s^{-1} is indicative of pore particle diffusion as the rate determining step. In this investigation, the values of $\overline{D}$ were 1.04×10^{-8} cm^2 s^{-1} and 5.2×10^{-9} cm^2 s^{-1} in the presence and absence of ultrasound, respectively. As these amounts are larger than 10^{-11} cm^2 s^{-1}, then the pore diffusion in the sorption process is not the only rate-limiting step and some other steps may be involved [22,23]. The pore diffusion coefficient can be determined using the model of Weber and Morris [9,24]:

$$q = \frac{K_w}{W}(t^{1/2}) \quad (5)$$

$$W = \frac{(C_o - C_t)}{q} \quad (6)$$

where C_o is the initial concentration (mg l^{-1}), C_t is the concentration at any time (mg l^{-1}), t is the time (min), q is the amount of sorption at any time (mg g^{-1}), W is the weight of sorbent per volume of reactor (g l^{-1}) and k_w is the Weber pore diffusion coefficient (mg l^{-1} min$^{-1/2}$). The values of k_w were determined from the plots of q versus $t^{1/2}$ and it was tabulated in Table 5.

Table 6
Film diffusion coefficient in the presence of ultrasound and stirring

T (°C)	Stirring			Ultrasound			$\frac{k_f}{k_f}$
	k_f (cm s^{-1}).10^6	R^2	$\frac{k_f}{k_{f30}}$	k_f (cm s^{-1}).10^6	R^2	$\frac{k_f}{k_{f30}}$	
30	1.83	0.99	1.00	5.01	0.99	1.00	2.73
40	3.77	0.99	2.06	7.97	0.99	1.60	2.10
50	6.02	0.99	1.60	9.90	0.99	1.97	1.64

The film diffusion coefficient can be determined [9] from the initial slope of the curves C_t/C_o versus time (Table 6). The values of porous and film diffusion coefficients obtained in the presence of ultrasound were 1.3–1.8 and 1.6–2.7 times greater than the absence of ultrasound, respectively. This behavior could be attributed to the induced turbulence and additional convective mass transport inside the pores and at the surface caused by micro-jets [14]. There is also an increase in porous and film diffusion coefficients by increasing the temperature in both the presence and the absence of ultrasound (Tables 5 and 6). This enhancement could be attributed to the higher mobility of ions and mass transfer at higher temperatures for both mentioned methods.

4. Conclusion

Discarded tire rubber can be used as a cheap sorbent for the removal of cadmium from aqueous solution. The maximum metal sorption capacity was found to be greater in the presence than in the absence of ultrasound. The experimental data properly fit the Langmuir model in the presence and absence of ultrasound. The sorption kinetics was first-order and the internal porous and film diffusions were important steps in the sorption mechanism.

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